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THE CRYSTAL STRUCTURES OF TANTALITE, IXIOLITE AND WODGINITE FROM BERNIC LAKE, MANITOBA
I. TANTALITE AND IXIOLITE

J. D. GRICE*, R. B. FERGUSON AND F. C. HAWTHORNE
Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structures of manganotantalite and ixiolite from the Tanco pegmatite, Bernic Lake, Manitoba have been refined using Mo$K\alpha$ radiation and 3-dimensional 4-circle diffractometer data to final R_w values of 8.4% and 8.9% respectively. Tantalite: orthorhombic *Pbcn*, *a* 14.413(3), *b* 5.760(1), *c* 5.084(1)Å, $Z=4[AB_2O_6]=4[(Mn_{0.97}Ti_{0.02}Fe^{2+}_{0.01}Sn_{0.002})(Ta_{0.64}Nb_{0.36})_2O_6]$. The structure of Sturdivant (1930) is confirmed. The mean octahedral *A*(Mn)–O distance is 2.18(4) and *B*(Ta)–O is 2.01(3)Å, both in close agreement with the relevant radii sums, 2.19 and 2.00Å respectively. Pauling bond strengths to the three oxygens O(1), O(2) and O(3) are very poor (2, 1½, 2½ v.u.), but when account is taken of the distance–distortion of the octahedra (especially *B*) by distributing the bond strengths inversely as the 5th power of the cation-oxygen distance (Pyatenko 1973), the three oxygens receive 2.04, 1.99 and 1.97 v.u. respectively.

Ixiolite is orthorhombic *Pbcn*, *a* 4.785(2) ($\sim\frac{1}{3}a_{tant.}$), *b* 5.758(2), *c* 5.160(2)Å, $Z=4[(Ta_{0.42}Mn_{0.30}Nb_{0.24}Ti_{0.02}Sn_{0.005}Fe^{2+}_{0.002})O_2]$. The structure is that of a cation-disordered tantalite with all metals in one special site 4*M* and all oxygens in one general site 8O. The structure type is α–PbO_2. Some symmetry elements correspond to true, and others to pseudo-symmetry elements in tantalite. The mean octahedral *M*-O distance is 2.06(4)Å, in close agreement with the sum of the oxygen and weighted mean cation radii (2.04Å).

SOMMAIRE

Les structures cristallines de la manganotantalite et de l'ixiolite ont été affinées, sur spécimens provenant de la pegmatite de Tanco, Bernic Lake, Manitoba, à l'aide de données tridimensionnelles obtenues au rayonnement Mo$K\alpha$ sur diffractomètre à quatre cercles, jusqu'au résidu pondéré final R_w de 8.4% et 8.9% respectivement. La tantalite est orthorhombique *Pbcn*, *a* 14.413(3), *b* 5.760(1), *c* 5.084(1)Å, $Z=4[AB_2O_6]=4[(Mn_{0.97}Ti_{0.02}Fe^{2+}_{0.01}Sn_{0.002})(Ta_{0.64}Nb_{0.36})_2O_6]$. La structure établie par Sturdivant (1930) est confirmée. La longueur moyenne des liaisons *A*(Mn)–O est 2.18(4) et celle des liaisons *B*(Ta)–O, 2.01(3)Å; elles concordent chacune avec la somme des rayons ioniques, 2.19 et 2.00Å, respectivement. La somme des valences de liaison (Pauling) qui aboutissent aux atomes d'oxygène O(1), O(2) et O(3) est peu précise (2, 1½ 2½ u.v., respectivement), mais lorsqu'on tient compte de la distorsion des longueurs dans l'octaèdre (celui de *B* en particulier) en considérant la valence de liaison comme inversement proportionnelle à la 5^e puissance de la distance cation-oxygène (Pyatenko 1973), les atomes d'oxygène reçoivent 2.04, 1.99 et 1.97 u.v., respectivement.

L'ixiolite est orthorhombique *Pbcn*, *a* 4.785(2) ($\sim\frac{1}{3}a_{tant.}$), *b* 5.758(2), *c* 5.160(2)Å, $Z=4[(Ta_{0.42}Mn_{0.30}Nb_{0.24}Ti_{0.02}Sn_{0.005}Fe^{2+}_{0.002})O_2]$. Sa structure est celle d'une tantalite à cations désordonnés avec tous les métaux dans une même position spéciale 4*M* et tout l'oxygène en position générale 8O. La structure est du type α–PbO_2. Certains éléments de symétrie de l'ixiolite correspondent, dans la tantalite, à des éléments de symétrie vraie; d'autres, à des éléments de pseudo-symétrie. La longueur moyenne des liaisons *M*-O, 2.06(4)Å, concorde avec la somme 2.04Å du rayon ionique de l'oxygène et de la moyenne pondérée des rayons cationiques.

(Traduit par la Rédaction)

DEDICATION

It is a pleasure to include this pair of papers on the structures of three tantalum oxide minerals in the number of The Canadian Mineralogist dedicated to our colleague and friend, Leonard G. Berry, whose advice regarding certain aspects of this work we gratefully acknowledge.

INTRODUCTION

Tantalite, ixiolite and wodginite are three closely related orthorhombic or pseudo-orthorhombic tantalum oxide minerals, all of which occur in the Tanco pegmatite at Bernic Lake, Manitoba. The prototype tantalite (columbite)[1] has the ideal formula $FeTa_2O_6(FeNb_2O_6)$; the general formula may be written as AB_2O_6 where $A=(Fe^{2+},Mn)$ and $B=(Ta,Nb)$ with other elements, particularly Sn and Ti, substituting in *A* and/or *B*. Upon heating, some ixiolites give the X-ray powder pattern of olovotantalite

*Present address: Mineral Sciences Division, National Museum of Natural Sciences, Ottawa, Ontario, K1A 0M8.

(Nickel *et al.* 1963a,b) or wodginite (Khvostova & Maximova 1969) whereas others give the pattern of columbite-tantalite (Nickel *et al.* 1963b). The latter authors suggested that only the first be regarded as true ixiolites, and they tentatively suggested the name 'pseudo-ixiolite' for the second. There appears to be distinct chemical differences between these two types, with ixiolite/olovotantalite/wodginite generally containing more $Fe^{3+}/Sn^{4+}/Ti^{4+}$ than 'pseudo-ixiolite'/columbite-tantalite (Nickel *et al.* 1963b; Černý, pers. comm.). On the basis of cell dimensions, Nickel *et al.* (1963a,b) proposed that 'pseudo-ixiolite' is a cation–disordered columbite-tantalite with the general formula $(A,B)_3O_6$, or more simply $(A,B)O_2$, and that wodginite is a monoclinic pseudo-orthorhombic derivative of columbite-tantalite with the same simplest general formula as pseudo-ixiolite, $(A,B)O_2$. Grice *et al.* (1972) have described the detailed chemistry and crystal geometry of tantalite, 'pseudo-ixiolite' and wodginite from the Tanco pegmatite, confirming the proposals of Nickel *et al.* (1963a,b). As 'pseudo-ixiolite' has never been approved as a valid species by the IMA Commission on New Minerals and Mineral Names, we use the name ixiolite throughout the rest of this paper.

Because different settings have been variously used for the cells of these minerals by different authors, Table 1 (modified from Grice *et al.* 1972) summarizes this information. A background to the present work is provided by the following points that may be made from Table 1 and Figure 1:

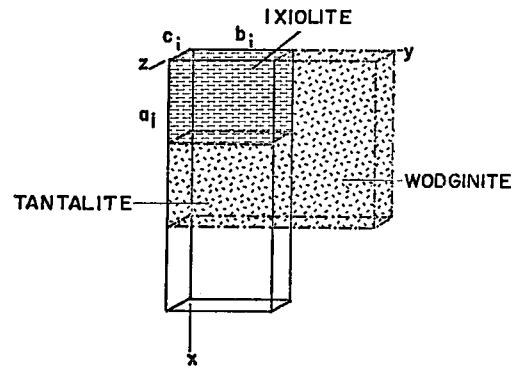


FIG. 1. Relative unit cells of ixiolite (a_1,b_1,c_1), tantalite and wodginite.

(1) the setting used for tantalite in the present study is that used by Strunz & Tennyson (1970) and Grice *et al.* (1972); this differs from the setting used by Sturdivant (1930) and Nickel *et al.* (1963a);

((2) the true cell of tantalite has $a \sim 14.4$, $b \sim 5.8$, $c \sim 5.1$Å and a cell content of $A_4B_8O_{24}$, but there exists a fairly distinct subcell with $a' \sim 4.8$Å$\sim a/3$, $b'=b$, $c'=c$ and a cell content of $\frac{1}{3}(A_4B_8O_{24})$. Although this cell is never used to describe tantalite, it is important as it corresponds to the true cell of ixiolite;

(3) Nickel *et al.* (1963b) and Grice *et al.* (1972) respectively showed that ixiolite has a cell whose b and c dimensions correspond to those of columbite-tantalite but whose $a \sim 4.8$Å $\sim \frac{1}{3}a$ of tantalite;

(4) Sturdivant (1930) showed that in the structure of columbite-tantalite, the 4*A* cations are in one site and the 8*B* cations in another so that it is a cation-ordered structure;

(5) Nickel *et al.* (1963b) showed that in the smaller ixiolite cell, there is only one site available for all the cations; hence this mineral,

[1]The tantalite/columbite cation-ordered structure may be regarded as the prototype of these three minerals because it was the first to be solved (Sturdivant 1930); however, from a structural viewpoint, the cation-disordered structure of ixiolite with the smaller cell and the same structure as α-PbO_2 (see for example Wyckoff 1963, p. 259) should be regarded as the prototype.

TABLE 1. CRYSTALLOGRAPHIC SETTINGS FOR IXIOLITE, COLUMBITE/TANTALITE, AND WODGINITE

		Ixiolite			Columbite/Tantalite					Wodginite		
		These papers & refs. 2,4b,5*	ref. 3	ref. 4a	true cell	subcell	These papers & refs. 2,5,7*	ref. 6	ref. 3.4a	true cell	subcell	These papers & refs. 1.2.3.4a.5*
Axial lengths, Å	4.8	a	a	b	14.4	(x1/3=)4.8	$a(a')$	b	$b(b')$	9.5	(x1/2=)4.8	$a(a')$
	5.8	b	b	a	5.8	5.8	b	a	a	11.5	(x1/2=)5.8	$b(b')$
	5.2	a	a	a	5.1	5.1	a	a	a	5.1	5.1	a
β°	(90)				(90)	(90)				∿91°	∿91°	
V(V'), Å3	140				423	(x1/3=)141				556	(x1/4=)139	
Space group		*Pbcn*	*Pnab*	*Pcan*			*Pbcn*	*Pnaa*	*Pccn*			*C2/c*(*P2/c*) or *Cc*†(or *Pc*)
Ideal cell content Z (Z')**		$(A_4B_8C)_4O_8$			$A_4B_8O_{24}$	$1/3[A_4B_8O_{24}]$				$A_4(C>A,B)_4B_8O_{32}$	$1/4[A_4(C>A,B)_4B_8O_{32}$	

*References: (1)Graham & Thornber (1974); (2)Grice *et al.* (1972); (3)Nickel *et al.* (1963a); (4a)Nickel *et al.* (1963b), Fig. 3, Table 4; (4b)Nickel *et al.* (1963b), positional parameters (p. 973); (5)Strunz *et al.* (1970); (6)Sturdivant (1930); (7)Wyckoff (1965).
**A=Fe,Mn; B=Nb,Ta; C=Sn,Ti(mainly).
†The present work (Paper II) shows that the space group is *C2/c*. See text.

with cell contents $(A,B)_4O_8$ must have a cation-disordered structure. Such a structure is the same as α–PbO_2 (Wyckoff 1963, p. 259);

(6) the cells of both tantalite and wodginite can be regarded as (different) supercells of ixiolite which may thus be taken as the prototype structure of these three minerals.

In order to completely characterize the interrelationship of tantalite and ixiolite, and of both to the closely related wodginite, the crystal structures of all three minerals have been refined. The results for tantalite and ixiolite are presented here, and for wodginite in Part II of these papers.

Previous Work

The crystal structure of columbite was solved by Sturdivant (1930), and the similarity of the powder patterns of columbite and tantalite suggested that they are isostructural. However, there has been no complete modern refinement of either structure although we understand that E. E. Foord of Stanford University (private communication to P. Černý, 1975) has recently refined a columbite structure. In addition, there has been no single-crystal structure study of ixiolite; however, Nickel *et al.* (1963b) proposed a structure for ixiolite based on that of columbite, and they confirmed it by the calculation of intensities on powder photographs.

The specimens of the three minerals selected for the present study are from the Li-Cs-Be Tanco pegmatite at Bernic Lake, Manitoba, where, together with microlite, they constitute the Ta-bearing ore minerals. The petrologic setting and mineralogy of the pegmatite are described in detail elsewhere (*Can. Mineral. 11*, Pt. 3, 1972).

Experimental

The specimens chosen for the structure analyses were those considered most suitable on the basis of their crystal perfection, composition and presumed ordering or disordering of the cations. The specimens are described by Grice *et al.* (1972) from which the chemistry, space group and other characteristics have been taken and reproduced, along with some of the present results, in Tables 2 and 4. The composition for tantalite given in Table 2 is slightly different from that given in Grice (1973) in that the total of (Mn+Ti+Fe+Sn) has been normalized to 4.00 to satisfy requirements of the structure. The groupings of the cations in the chemical formulae in both tables express the cation distributions deduced from the structure analyses as explained below. The cell dimensions given in these tables differ slightly from those given previously because the latter are from refined powder data for a relatively large amount of material whereas the former are from single-crystal diffractometer measurements on the actual crystal analyzed. It can be seen from the composition given in Table 2 that the tantalite is Mn-rich and Fe-poor and hence it is strictly a manganotantalite; however, for brevity it will be referred to in this paper as "tantalite".

Tantalite

Nickel *et al.* (1963b) showed that heating seems to enhance the cation ordering in columbites. Although precession photographs indicated that the sample chosen for the structure refinement (G69-58, Grice *et al.* 1972) was fairly ordered, an attempt was made to increase this ordering by heating. Crystals were heated at 1000°C for 16 hours at $F(O_2)=10^{-14}$ atmospheres; the intensification of certain critical reflections after heating suggested that cation ordering had increased. Ground spheres of this heated specimen were found to give unsatisfactory reflections because the grinding developed incipient parting planes, and thus a heated blocky polyhedral fragment $0.33\times0.22\times0.17$mm was used for the collection of the intensity data. The crystal was mounted for rotation about a reciprocal axis normal to a cleavage plane, this axis subsequently proving to be [310]*, and the bounding planes were assigned Miller indices for subsequent absorption corrections.

Intensities were collected using Mo/Zr radiation on a Picker FACS 1 diffractometer in the Dept. of Biochemistry, University of Alberta. Cell dimensions derived from the diffractometer measurements are given in Table 2. A total of 615 reflections was collected over one octant of reciprocal space out to $2\theta(MoK\alpha)$ 60° assuming no space-group extinctions. A few reflections were observed that violated the space-group extinctions for *Pbcn*; these were assumed to be due to the Renninger effect although Khvostova & Maximova (1969) and Sidorenko *et al.* (1971) report that the powder patterns of some columbite-tantalites and ixiolites show a few reflections that violate the space-group extinctions for *Pbcn* (in the present setting). As it is impossible to observe Renninger effects in a powder pattern, these reflections cannot be thus explained. However, our structure appears to refine fairly satisfactorily in *Pbcn* and we can offer no explanation for the results of the Russian authors.

TABLE 2. TANTALITE: CHEMICAL, PHYSICAL, CRYSTALLOGRAPHIC AND STRUCTURAL DATA

From Grice et al. (1972): specimen G69-58

Cell content: $4[(Mn^{2+}_{0.97}Ti^{4+}_{0.02}Fe^{2+}_{0.01}Sn^{4+}_{0.00_2})(Ta^{5+}_{1.28}Nb^{5+}_{0.72})O_6^{2-}]$

Specific gravity: measured 6.76, calculated 7.073

Space group: *Pbcn* (no. 60)

From the present work: a=14.413(3), b=5.760(1), c=5.084(1)Å, V=422.1Å

Note: upper entries are from Sturdivant (1930); lower entries are the present work.

		x	y	z	B(Å^2)
A=Mn	4c	0	0.350	1/4	–
		0	0.322(2)	1/4	0.63(21)
B=Ta	8d	0.163	0.175	0.750	–
		0.1628(2)	0.1770(3)	0.7367(4)	0.64(15)
O(1)	8d	0.090	0.095	0.083	–
		0.099(2)	0.094(5)	0.055(6)	0.4(4)
O(2)	8d	0.410	0.100	0.083	–
		0.419(2)	0.112(6)	0.108(7)	1.3(5)
O(3)	8d	0.750	0.080	0.070	–
		0.758(2)	0.121(5)	0.099(6)	0.9(5)

	β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B	13(1)	44(4)	24(5)	0(4)	1(4)	0(11)

* $\beta_{ij} \times 10^4$

$R(Z)=\Sigma(|F_{obs}|-|F_{calc}|)/\Sigma|F_{obs}|$;

$R_w(Z)=[\Sigma w(|F_{obs}|-|F_{calc}|)^2/\Sigma wF^2_{obs}]^{\frac{1}{2}}$, w=1

Absorption corrections for polyhedral crystal shape were performed using the program GONO9 (written by the late W. C. Hamilton of Brookhaven National Laboratory). Data reduction was performed with DATAP5 (program from the Weizmann Institute, Israel). Of the 615 reflections measured, 602 were considered as observed, the criterion for an observed reflection being that its magnitude exceeded three standard deviations based on counting statistics.

The cell of tantalite has the content $A_4B_8O_{24}$ where, for this tantalite, A=Mn,Ti,Fe,Sn and B=Ta,Nb. The initial positional parameters were taken from Sturdivant (1930); the A site was initially assumed to be pure Mn^{2+} and the B site to be (⅝ Ta + ⅜ Nb) to which the composition approximates. Scattering factors for fully ionized atoms (except Ta where only the neutral atom values are given) were taken from Cromer & Mann (1968). Structure refinement was carried out using the programs of Larson (1971).

During the refinement, a number of problems arose: (1) anomalies on the ρ_o–ρ_c map which suggested a "splitting" of the Ta-site atom; (2) the F_c values for certain groups of reflections, mainly of the type 00*l*, 0*kl* and 3*ll*, agreed poorly with the F_o values; (3) the weighted R was considerably higher than the unweighted; and (4) the isotropic temperature factor of the O(2) oxygen was considerably higher (3.98Å^2) than for O(1) and O(3), (0.53 and 0.44Å^2). The detailed progress of the refinement and a description of how these problems were handled are given by Grice (1973). Various attempts were made to resolve the problems, but it proved to be impossible to do so satisfactorily. We feel that most or all of them arose from the very high absorption of this crystal (μ=390cm^{-1}) together with the problem of accurately measuring the dimensions of the crystal.

An attempt was made during the analysis to refine on a cation distribution which assumed an interchange of some Mn^{2+} and Nb^{5+} between the A and B sites for which an argument can be made on the basis of bond strengths (Grice 1973; Grice & Ferguson 1974). However, this resulted in no significiant improvement in the R-factor, and we now reject this model.

After exploring various structural possibilities, including both isotropic and anisotropic temperature factors for both cations and oxygens, we concluded that the most realistic model is one with the A site occupied by all the Mn plus the minor amounts of Ti,Fe and Sn, and the B site by all the Ta and Nb (see Table 2), with anisotropic temperature factors for the cations and isotropic temperature factors for the anions. For this model, R=9.8% and R_w=8.4% (Table 2), and accordingly it was adopted as the best model for this tantalite*. Table 2 gives the final atomic parameters for this model together with the positional parameters of columbite (Sturdivant 1930) for comparison.

Interatomic distances and angles calculated with the program DISAGL (Larson 1971) are listed in Table 3. Projections of the structures are given in Figure 1a,b.

Ixiolite

The ixiolite selected for the structure analysis (G69-55, Grice *et al.* 1972) was chosen because of its chemical similarity to tantalites from the same deposit, and because precession photographs showed none of the supercell reflections characteristic of a transition from cation-disordered ixiolite to cation-ordered tantalite (Grice 1970).

As with the tantalite specimen, ground spheres of this ixiolite gave poor X-ray reflections, and

*Complete set of structure factor tables is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

TABLE 3. TANTALITE: INTERATOMIC DISTANCES AND INTERBOND ANGLES

Equivalent Position Code			
a	x	y	z
b	½-x	½-y	½+z
c	x	-y	½+z
d	x	y	1+z
e	1-x	-y	1-z
f	1-x	y	½-z
g	½+x	½-y	1-z
h	-x	y	½-z
i	x-½	½-y	-z
j	x-½	½+y	½-z
k	x-½	½-y	1-z
m	½-x	½+y	z

A(Mn)-O distances			
A a	-O(1)a	x 2	2.18(3)Å
	-O(2)b	x 2	2.20(4)
	-O(2)j	x 2	2.16(4)
		mean	2.18(2)Å

B(Ta)-O distances			
B a	-O(1)c	x 1	2.04(3)Å
	-O(1)d	x 1	1.92(3)
	-O(2)b	x 1	1.81(4)
	-O(3)e	x 1	2.23(3)
	-O(3)f	x 1	2.08(3)
	-O(3)k	x 1	1.98(3)
		mean	2.01(1)Å

O-O distances around A(Mn)			
O(1)a-O(1)h	x 1	3.47(6)Å	
O(1)a-O(2)b	x 2	3.29(5)	
O(1)a-O(2)i	x 2	3.21(4)	
O(1)a-O(2)m	x 2	3.01(4)	
*O(2)b-O(2)j	x 2	2.89(7)	
O(2)b-O(2)m	x 2	2.85(3)	
O(2)j-O(2)m	x 1	2.76(7)	
	mean	3.06(2)	

O-O distances around B(Ta)		
O(1)c-O(1)d	x 1	2.76(2)Å
O(1)c-O(2)b	x 1	2.80(4)
O(1)c-O(3)e	x 2	2.72(4)
*O(1)c-O(3)f	x 2	2.54(4)
O(1)d-O(2)b	x 1	2.84(4)
O(1)d-O(3)k	x 1	2.93(4)
O(2)b-O(3)f	x 1	2.98(5)
O(2)b-O(3)k	x 1	2.94(5)
O(3)e-O(3)f	x 1	2.90(3)
O(3)f-O(3)k	x 1	2.95(3)
	mean	2.80(1)

O-A(Mn)-O angles		
O(1)a-A-O(1)h	x 1	106(2)°
O(1)a-A-O(2)b	x 2	98(1)
O(1)a-A-O(2)i	x 2	94(1)
O(1)a-A-O(2)m	x 2	88(1)
*O(2)b-A-O(3)j	x 2	83(1)
O(2)b-A-O(3)m	x 2	82(1)
O(2)j-A-O(3)m	x 1	79(2)
	mean	89.6(6)

O-B(Ta)-O angles		
O(1)c-B-O(1)d	x 1	88(1)°
O(1)c-B-O(2)b	x 1	93(1)°
O(1)c-B-O(3)e	x 2	79(1)°
*O(1)c-B-O(3)f	x 2	76(1)°
O(1)d-B-O(2)b	x 1	99(1)°
O(1)d-B-O(3)k	x 1	97(1)°
O(2)b-B-O(3)f	x 1	100(1)°
O(2)b-B-O(3)k	x 1	102(1)°
O(3)e-B-O(3)f	x 1	84(1)°
O(3)f-B-O(3)k	x 1	93(1)°
	mean	88.8(3)

*denotes shared octahedral edge

TABLE 4. IXIOLITE: CHEMICAL, PHYSICAL, CRYSTALLOGRAPHIC AND STRUCTURAL DATA

From Grice et al. (1972): Specimen G69-55

Cell Content $4[(Ta^{5+}_{0.42}Mn^{2+}_{0.30}Nb^{5+}_{0.24}Ti^{4+}_{0.02}Sn^{4+}_{0.00_5}Fe^{2+}_{0.00_2})O^{2-}_2]$

Specific gravity: measured 6.94(3), calculated 6.95

Space group *Pbcn* (no. 60)

From the present work: $a = 4.785(2)$, $b = 5.758(2)$, $c = 5.160(2)$Å,

$V = 142.2$Å^3

		x	y	z	B(Å²)
M	4c	0	0.3317(8)	1/4	2.3(1)
O	8d	0.7224(83)	0.1217(69)	0.4158(75)	2.8(7)

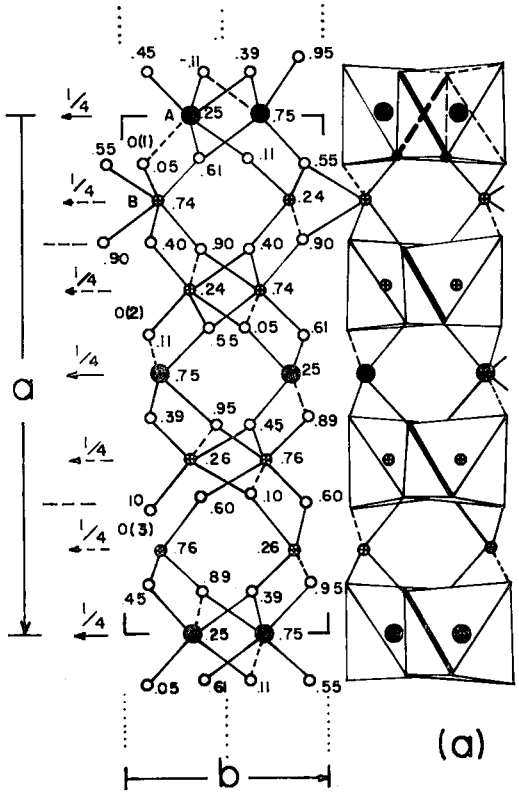
	β11*	β22	β33	β12	β13	β23
M	53(3)	6(1)	13(2)	0	-3(6)	0

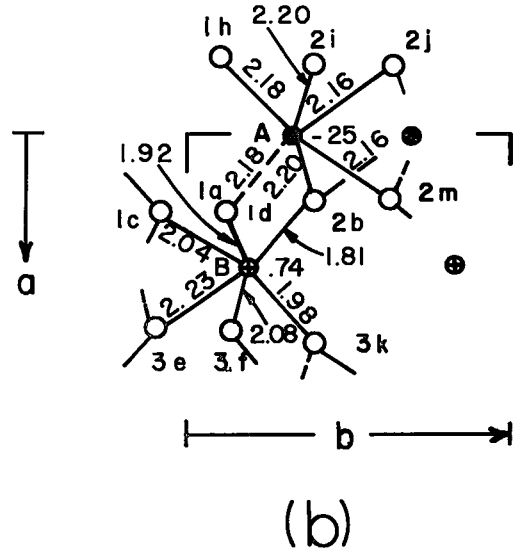
*$\beta_{ij} \times 10^3$

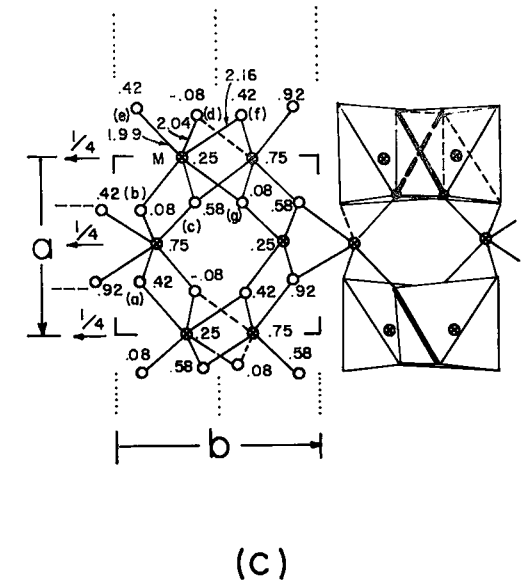
so a polyhedral fragment ($0.15 \times 0.20 \times 0.20$mm) was again chosen in this case, and its bounding planes identified for computing absorption corrections. This fragment was mounted for rotation normal to the largest cleavage plane, the rotation axis subsequently proving in this case to be [100]*. Data collection was carried out using Mo/Zr radiation on the Picker FACS I diffractometer in the Department of Geology, University of Toronto. The cell dimensions derived from the FACS I measurements are given in Table 4, and they are presumed to have standard deviations of ~0.002Å. The slight differences in these cell dimensions from those given for the same specimen (unheated) by Grice *et al.* (1972) are presumably due, as in the case of tantalite, to the different material (single-crystal versus powder) used for the two determinations.

Initially the intensities of a number of reflections possible for the larger direct cell of tantalite but forbidden for the smaller cell of ixiolite were measured. These proved to be of negligible intensity, and so we concluded that this crystal closely approximates the small cell characteristic of cation-disordered ixiolite. The space group deduced by Nickel *et al.* (1963b), *Pbcn*, was confirmed. A complete data collection out to $2\theta(MoK\alpha)$ 50° was then carried out in the two octants *hkl* and $\bar{h}kl$ of reciprocal space. As with tantalite, the absorption corrections were severe with $\mu = 390$cm^{-1}. Equivalent relative F_o's for the two octants were averaged, and weighted on the basis of the magnitudes of the F_o's and the agreement of the F_o's between the two octants, resulting in 126 unique observed reflections.

As indicated in point (5) of the Introduction, Nickel *et al.* (1963b) concluded that, on the basis of X-ray diffraction data and composition, ixiolite must have a structure that is essentially that of a cation-disordered columbite–tantalite. Grice *et al.* (1972) showed that the material referred to as 'pseudo–ixiolite' has the same space group and approximately the same cell dimensions as ixiolite. Nickel *et al.* (1963b) then showed that, with cell contents of $(A,B)_4O_8$ and $A_4B_8O_{24}$ for ixiolite and tantalite respectively, the equivalent positions in their common space group *Pbcn* (in our setting) (Tables 2 and 4) are such that one 4-fold cation site in ixiolite must be equivalent to the one 4-fold plus one 8-fold cation site in tantalite (with three times the volume), and that one 8–fold oxygen site in ixiolite must be equivalent to the three different 8-fold oxygen sites in tantalite. On this basis they proposed a structure for ixiolite in which the parameters of the one cation and of the one oxygen are the averages of the parameters of the different corresponding cations and oxygens, of the columbite structure. Powder-pattern intensities that they calculated for this ixiolite structure are in good qualitative







LEGEND

SHARED OCTAHEDRAL EDGES

SHARED OXYGEN

b– GLIDE

c– GLIDE

TRUE 2

PSEUDO 2

A(Mn) CATION

B(Ta) CATION

TANTALITE

M CATION IXIOLITE

OXYGEN

FIG. 2. Projections of the structures of tantalite and ixiolite along *z*. **2(a)**: Tantalite. Prototype atoms are labelled *A*(=Mn), *B*=(Ta,Nb), O(1), O(2), O(3). Shown are some chains of staggered *A*-O and *B*-O octahedra parallel to *z* seen end-on. Shared octahedral edges and shared oxygens are distinguished in the upper part of the polyhedral representation. **2(b)**: Enlargement of the upper part of 2(a) showing the octahedral *A*-O and *B*-O distances (Å) in tantalite. Oxygen types designated as in Table 3. **2(c)**: Ixiolite. Prototype single cation labelled M and single oxygen labelled (a); other oxygens designated as in Table 5. One-half of the octahedral *M*-O distances are shown, the other equivalent ones being related by the 2-fold axis at 0,*y*,¼. The staggered octahedral chains are analogous to those in tantalite although in ixiolite all chains are alike.

agreement with the observed intensities. Following Nickel *et al.* (1963b), the cation was placed at 0,0.32, ¼; the scattering curve used was that of neutral Ta (Cromer & Mann 1968) modified by a fixed occupancy factor (0.386) to take account of the other cations occupying this site (see Table 4). Difference Fourier syntheses following three cycles of least-squares refinement located the positions of all oxygens. Least-squares refinement of all variables with anisotropic temperature factors for the cation and isotropic temperature factors for the anion resulted in convergence at $R=14.0\%$ and $R_w=8.9\%$. Final atomic parameters are given in Table 4, the interatomic distances and angles in Table 5, and a projection of the structure in Figure 1c.

TABLE 5. IXIOLITE INTERATOMIC DISTANCES & INTERBOND ANGLES

Equivalent Position Code

a	x	y	z
b	1-x	y	½-z
c	x-½	½-y	1-z
d	½-x	½-y	z-½
e	x-1	y	z
f	½-x	½+y	z
g	x-½	½+y	½-z

O-M-O angles

0 b -M-0 d	x 2	94(1)°
0 b -M-0 e	x 1	105(2)°
0 d -M-0 e	x 2	95(1)°
0 d -M-0 f	x 2	89(1)°
*0 d -M-0 g	x 2	80(2)°
0 e -M-0 f	x 2	88(1)°
0 f -M-0 g	x 1	79(2)°
	mean	89.7(3)

M-O distances

M-0 d	x 2	2.04(4)Å
-0 e	x 2	1.99(4)
-0 f	x 2	2.16(4)
mean M-0		2.06(2)Å

O-O distances around M

0 b -0 d	x 2	2.94(5)Å
0 b -0 e	x 1	3.16(8)
0 d -0'e	x 2	2.99(4)
0 d -0 f	x 2	2.94(4)
*0 d -0 g	x 2	2.69(8)
0 e -0 f	x 2	2.89(1)
0 f -0 g	x 1	2.73(8)
mean		2.90(3)Å

*denotes shared edge

Discussion: Tantalite

Structural features. In his original derivation of the columbite structure, Sturdivant (1930) described the structural principles of this mineral, and these may be seen from a consideration of the projection of the structure along *z* shown in Figure 2a. The oxygen anions are in pseudo-hexagonal closest packing parallel to (100), and the metal cations occupy one-half of the available (pseudo-) octahedral interstices. In the idealized structure $MnTa_2O_6(AB_2O_6)$, the two different cations Mn and Ta are ordered into different octahedral sites (*A* and *B* respectively) in the required ratio of 1:2 so that they also occur in layers parallel to (100) with layers of Mn(*A*) cations at $x=0$ and ½, and of Ta(*B*) cations at $x=1/6$, 2/6, 4/6 and 5/6. In terms of the linking of cation-oxygen octahedra, the structure can be regarded as chains of staggered octahedra running parallel to *z* with any one chain containing, in the ideal structure, only Mn(*A*) or Ta(*B*) cations in the centres of the octahedra, and with one layer of Mn(*A*) chains followed by two layers of Ta(*B*) chains. In any one chain, one octahedron shares one edge with the octahedron above it and one with the octahedron below it along *z*, and any one chain is linked to its neighboring parallel chains through certain octahedral corners (oxygens) (Fig. 2a). This octahedral linking is such that each oxygen is coordinated by three cations.

From Figure 2b and Table 3 one can see that the mean octahedral *A*-O distance is 2.18(2)Å with variations from 2.16(4) to 2.20(4)Å, and the mean octahedral *B*-O distance is 2.01(1)Å with variations from 1.81(4) to 2.23(3)Å. The O-O distances around *A* and *B* vary from 2.76(7) to 3.47(6)Å and from 2.54(4) to 2.98(5)Å respectively, with mean values of 3.06(2) and 2.80(1)Å. The mean cation-oxygen distances agree well with the sums of the radii of the particular ions as given by Shannon & Prewitt (1969, 1970): $^{VI}Mn^{2+} - {}^{III}O^{2-} = 0.83+1.36=2.19$Å and $^{VI}(Ta,Nb)^{5+} - {}^{III}O^{2-} = 0.64+1.36=2.00$Å, compared with observed values of 2.18(4)Å and 2.01(3)Å respectively.

Certain individual distances of both the *A*-O and *B*-O octahedra differ significantly from their mean values, and provide a measure of the distortion of the structure from ideal hexagonal closest packing of the oxygens with an ideal occupancy of certain octahedral interstices by cations. Another measure of the distortion is the departure of certain interbond angles from the ideal. One can see from Table 3 that certain O-*A*-O and *O*-*B*-O angles depart by as much as 16° and 14° respectively from the ideal value of 90°.

Figure 2(a,b) and Table 3 show that the shared edges of the *A*-O octahedron are the equivalent pair O(2)*i*-O(2)*m* and O(2)*b*-O(2)*j* with an O-O distance of 2.89(7)Å and an O-*A*-O angle of 83(1)°. The Table shows that both of these are among the smallest for the *A*-O octahedron so it may be said that this octahedron conforms fairly well to Pauling's third rule regarding the linking of coordination polyhedra which says that shared edges be shorter than unshared because of cation–cation repulsion. Similarly for the *B*-O octahedron, the shared edges are the equivalent O(1)*c*-O(3)*f* and O(1)*d*-O(3)*e* with an O-O distance of 2.54(4)Å and an O-*B*-O angle of 76(1)°. Table 3 shows that these are the smallest respective values for the *B*-O octahedron so that it also conforms to Pauling's third rule. This better agreement for the *B* site is to be expected because the *A* site contains mostly divalent cations (Mn^{2+}) where-

TABLE 6. BOND STRENGTHS IN THE TANTALITE STRUCTURE

See Fig. 2(a,b) and Table 3. All bond strengths in valence units (v.u.).

method of evaluation			Pauling (1929)			Ferguson (1974)			Pyatenko (1973)		
cation *A*(Mn)											
assumed charge			2+			2+			2+		
assumed A-O exponent			0*			1			5**		
cation *B*(Ta)											
assumed charge			5+			5+			5+		
assumed B-O exponent			0*			1			5		
anion	cation	anion-cation distance	v_{ij}	Σ	$\lvert\Delta\rvert^{\dagger}$	v_{ij}	Σ	$\lvert\Delta\rvert^{\dagger}$	v_{ij}	z	$\lvert\Delta\rvert^{\dagger}$
$III_{O(1)}$	Mn	2.18(3)Å	1/3	2	0	0.333	2.020(36)	0.020	0.333	2.044(493)	0.044
	Ta	2.04(3)	5/6			0.820			0.736		
	Ta'	1.92(3)	5/6			0.867			0.975		
$III_{O(2)}$	Mn	2.20(4)	1/2	1 1/2	1/2	0.330	1.588(39)	0.412	0.318	1.986(358)	0.014
	Mn'	2.16(4)	1/2			0.336			0.349		
	Ta	1.81(4)	5/6			0.921			1.319		
$III_{O(3)}$	Ta	2.23(3)	5/6	2 1/2	1/2	0.748	2.392(43)	0.392	0.466	1.970(667)	0.030
	Ta'	2.08(3)	5/6			0.802			0.660		
	Ta''	1.98(3)	5/6			0.842			0.844		
$\Sigma\lvert\Delta\rvert$					1			0.824			0.088

Total bond strengths (v.u.) to octahedral groups of 6 oxygens.

method	Pauling (1960)	Ferguson (1974)	Pyatenko (1973)
Around *A*(Mn)			
2 x O(1)	4	4.040	4.088
4 x O(2)	6	6.352	7.944
Σ	10	10.392	12.032
$\lvert\Delta\rvert'^{\dagger\dagger}$	2	1.608	0.032
Around *B*(Ta)			
2 x O(1)	4	4.040	4.088
1 x O(2)	1 1/2	1.588	1.986
3 x O(3)	7 1/2	7.176	5.910
Σ	13	12.804	11.984
$\lvert\Delta\rvert'^{\dagger\dagger}$	1	0.804	0.016
$\Sigma\lvert\Delta\rvert'(1A+2B)$	4	2.412	0.064

*Implying non-distance dependent relationship. **Pyatenko (1973) gives no exponent for Mn; we have assumed the value of 5.
†$\lvert\Delta\rvert = \lvert 2 - \Delta\rvert$ v.u. ††$\lvert\Delta\rvert' = \lvert 12 - \Delta\rvert$ v.u.

as *B* contains only pentavalent (Ta^{5+}, Nb^{5+}) cations.

Bond strengths. From Figure 2a and Table 6, it can be seen that each of the three oxygens is coordinated by three cations, O(1) by Mn,Ta and Ta′, O(2) by Mn,Mn′ and Ta, and O(3) by Ta,Ta′ and Ta″. In his original analysis of the columbite structure, Sturdivant (1930) noted that this structure shows a large deviation from ideal of the "electrostatic valences" (bond strengths) to the oxygens when evaluated according to the 2nd rule of Pauling (1929), regarding coordination polyhedra in ionic structures. Such Pauling bond strengths are non-distance-dependent, and are often referred to as formal bond strengths. These are shown for tantalite (columbite) in Table 6 under "Pauling (1929)" where it may be seen that these bond strengths to O(1),O(2), and O(3) are respectively 2, 1½ and 2½ v.u., resulting in $\Sigma|\Delta| = 1$ v.u. and indicating a very large imbalance. However, Sturdivant (1930) also suggested that the strong distortion of the octahedral oxygens around "Cb" was such as to compensate for this imbalance if the bond strength distribution were distance-dependent.

Since Pauling's paper of 1929, various authors have suggested different ways of evaluating bond strengths such that, in a distorted cation-anion polyhedron, the anions closer than the mean to the cation would receive greater than the formal bond strengths, and those further than the mean would receive less than the formal values. Among such procedures described recently are those by Brown & Shannon (1973), Pyatenko (1973) and Ferguson (1974). It is not possible to apply the fairly widely used bond-strength–bond-length curves of Brown & Shannon (1973) to the tantalite structure because they do not include (Ta,Nb)-O. The method of Pyatenko (1973) and that independently derived by Ferguson (1974) are similar in that they both assume ideal charges on the cations and they both distribute the bond strengths from the cations to the anions in amounts that are inversely proportional to some function of the cation-anion distance. In the method of Ferguson, this function is simply the distance itself, that is, an exponent of 1 (although Gait *et al.* 1970) had earlier applied the method to the structure of low albite using an exponent of 2). Table 6 shows under the heading 'Ferguson (1974)' the bond strengths to the three oxygens using an exponent of 1 for both octahedra, and calculated using the computer program VLBDDB described by Ferguson (1974) as modified by Hawthorne & Ferguson (1975). One can see that modifying the bond strength distribution

in this way does appreciably improve the bond strengths to the two oxygens, O(2) and O(3) whose formal bond strengths are seriously unbalanced. This improvement is reflected in the drop of $\Sigma|\Delta|$ from 1 to 0.824 v.u. These results, still very unsatisfactory, suggest that if the exponent were increased, the distribution would improve further. Pyatenko (1973) used much larger exponentials, and on the basis of evaluating the bond strengths in more than 20 structures, he derived exponentials applicable for different metals in metal-oxygen structures: 2.5 for Na,K; 6 for ^{IV}Al,Si, etc., and in particular 5 for Fe,Nb and Ta. In Table 6 under the heading "Pyatenko (1973)" are given the bond strengths for an exponent of 5 for both cations, also evaluated using the modified computer program VLBDDB. It may be seen that this large exponent gives rise to nearly ideal bond strengths to O(2) and O(3), 1.986 and 1.970 v.u., as well as to O(1), 2.044 v.u., the $\Sigma|\Delta|$ value being only 0.088 v.u. The very large standard deviations in the bond strengths evaluated in this way and given in the Table, arise from the large exponent combined with the method of evaluating the standard deviations. It is difficult to know what significance, if any, should be attached to such large standard deviations. Neglecting them, it may be said that the Pyatenko procedure using the large exponent of 5 for both sets of cation-oxygen distances appears to be a satisfactory one for evaluating the bond strengths in the tantalite structure.

In attempting to account for the very poor formal bond strengths to the oxygens in tantalite, Grice (1973) and Grice & Ferguson (1974), without knowledge of Pyatenko's procedure, proposed a partly-ordered structure for this tantalite, $(Mn^{2+}_{2.32}Nb^{5+}_{1.68})(Ta^{5+}_{5.12}Nb^{5+}_{1.20}Mn^{2+}_{1.68})O^{2-}_{24}$ which, because of strong absorption problems, could not be distinguished structurally from the ideal ordered structure, and which gave for an exponent of 1 ideal bond strengths (12 v.u.) to each of the two octahedral groups of oxygens (but not to the individual oxygens). This model is based on the assumption that differently-charged cations in a cation-disordered structure tend to order themselves, given the right conditions, in order to improve the bond strengths to the oxygens, and such an ordering would affect the oxygens as polyhedral groups and not just as individuals. However, we now reject this cation-partly-ordered model because of the good agreement described earlier between the two mean cation-oxygen distances and the radius sums, the unlikelihood of two such differently-sized and differently-charged cations being partly disordered to produce a stable structure, and now the satisfactory bond strengths to the three oxygens when evaluated using the cation-oxygen exponents of Pyatenko (1973).

In our final assessment of the bond strengths in tantalite we have summed them for octahedral groups of six oxygens (Table 6) in the manner just described using the three different methods. The mean Δ values per oxygen calculated this way are less than the means of the Δ values of the oxygens taken individually for each of the three methods and particularly for the Pyatenko method. However, the precision of the bond lengths and hence of the bond strengths is too low in this case to suggest whether the assessment of the bond strengths of the oxygens as individuals or as octahedral groups appears to be the more valid procedure.

Discussion: Ixiolite

If one considers the ixiolite structure in terms of the tantalite structure (rather than vice versa) which corresponds to the sequence of our analyses, then as indicated earlier (Introduction, points (5) and (6), and Tables 2 and 4), the ixiolite structure can be regarded as a substructure of the tantalite structure (Nickel *et al.* 1963b), It follows that the ixiolite structure (Fig. 2c) is characterized by the same close-packing of oxygens and linkages of the cation–anion octahedra as occur in the tantalite structure. With all cations in one site and all oxygens equivalent, the ixiolite structure has symmetry elements in certain positions that are only pseudo-symmetry elements in tantalite (cf. Fig. 1c with Fig. 1a). The mean cation-oxygen distance within the one cation-oxygen octahedron in ixiolite is 2.06(2)Å (Table 5), and this agrees well with the weighted mean for both of the octahedra in tantalite (Table 3), 2.07(1)Å and with the sum of the weighted cation and the oxygen radii of Shannon & Prewitt (1969, 1970), 2.04Å.

The mean of the octahedral O-O distances in ixiolite is 2.90(6)Å (Table 5), and this agrees with the weighted mean of the two groups of octahedral distances in tantalite (Table 3), 2.89(4)Å.

The shared octahedral edges in ixiolite are, of course, those corresponding to the shared edges in tantalite, namely the equivalent pair joining O*c*-O*f* and O*d*-O*g* (Fig. 2c and Table 5). These O-O pairs have a bond length of 2.69(8)Å and an O-*M*-O angle of 80(2)°, the former the shortest and the latter the second smallest of their octahedral groups, and so ixiolite, like tantalite, conforms well to the Pauling third rule.

Regarding bond strengths in ixiolite, for one-anion structures such as this, it follows that, provided the chemical formula is electrostatically balanced, the single anion must receive a total bond strength from the cation(s) that exactly equals its negative valence when the calculation is done by the simple non-distance-dependent Pauling method. The same condition holds for distance-dependent methods such as those of Pyatenko (1973) and Ferguson (1974) which assume ideal charges on the cations, and so a bond strength evaluation for ixiolite by any of these methods is meaningless.

Acknowledgments

Acknowledgments relating to this work are given at the end of the accompanying Part II paper.

References

See the References for the accompanying Part II paper.

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